Classops - [MoC 257 ACTIVE SOLID-STATE DEVICES (E.G., TRANSISTORS, SOLID-STATE DIODES)]

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April 2002 Patent Classification
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US-to-IPC Concordances by Cl
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Definitions By Tech Center
Schedules (MoC)
Definitions
US-to-IPC Concordances
US-to-Locarno Concordance
PDFs

499 **INTEGRATED CIRCUIT STRUCTURE WITH ELECTRICALLY ISOLATED COMPONENTS**

500 . Including high voltage or high power devices isolated from low voltage or low power devices in the same integrated circuit

501 . . Including dielectric isolation means

502 . . High power or high voltage device extends completely through semiconductor substrate (e.g., backside collector contact)

503 . With contact or metallization configuration to reduce parasitic coupling (e.g., separate ground pads for different parts of integrated circuit)

504 . Including means for establishing a depletion region throughout a semi- conductor layer for isolating devices in different portions of the layer (e.g., "JFET" isolation)

505 . With polycrystalline semiconductor isolation region in direct contact with single crystal active semiconductor material

506 . Including dielectric isolation means

507 . . With single crystal insulating substrate (e.g., sapphire)

508 . . With metallic conductor within isolating dielectric or between semiconductor and isolating dielectric (e.g., metal shield layer or internal connection layer)

509 . . Combined with pn junction isolation (e.g., isoplanar, LOCOS)

510 . . . Dielectric in groove

511 . . . . With complementary (npn and pnp) bipolar transistor structures)

512 . . . . . Complementary devices share common active region (e.g., integrated injection logic, I2L)

513 . . . . Vertical walled groove

514 . . . . . With active junction abutting groove (e.g., "walled emitter")

515 . . . . With active junction abutting groove (e.g., "walled emitter")

516 . . . . With passive component (e.g., resistor, capacitor, etc.)

517 . . . . With bipolar transistor structure

518 . . . . . With polycrystalline connecting region (e.g., polysilicon base contact)

519 . . . . Including heavily doped channel stop region adjacent groove

520 . . . . Conductive filling in dielectric-lined groove (e.g., polysilicon backfill)

521 . . . . Sides of grooves along major crystal planes (e.g., (111), (100) planes, etc.)

522 . . Air isolation (e.g., beam lead supported semiconductor islands)

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Document Title
Def 313 ELECTRIC LAMP AND DISCHARGE DEVICES

Search: lectrostatic NEAR(p) precipitators

History: MoC 257 ACTIVE SOLID-STATE DEVICE:

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Current Session Page 17/28

6/2002

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	U	1	Document ID	Issue Date	Pages	Title	Current OR	Current XRef	Retrieval C	Inventor	S	C	P	2	3		5	Imag
1	☑	☐	US 6402931 B1	20020611	18	Electrochemical machining using modulated reverse	205/659			Zhou, Chengdong et al.	☐	☐	☐	☐	☐	☐	☐	US (
2	☑	☐	US 6319384 B1	20011120		Pulse reverse electrodeposition for	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐	☐	☐	☐	☐	
3	☑	☐	US 6309528 B1	20011030		Sequential electrodeposition of metals using modulated	205/103	205/123; 205/125;		Taylor, E. Jennings et al.	☐	☐	☐	☐	☐	☐	☐	
4	☑	☐	US 6303014 B1	20011016		Electrodeposition of metals in small recesses using	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐	☐	☐	☐	☐	
5	☑	☐	US 6210555 B1	20010403		Electrodeposition of metals in small recesses for	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐	☐	☐	☐	☐	
6	☑	☐	US 6203684 B1	20010320		Pulse reverse electrodeposition for	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐	☐	☐	☐	☐	
7	☑	☐	US 6080504 A	20000627		Electrodeposition of catalytic metals using	429/42	205/103; 205/104;		Taylor, E. Jennings et al.	☐	☐	☐	☐	☐	☐	☐	
8	☑	☐	US 5804057 A	19980908		Method of removing metal salts from solution by	205/702	204/252; 204/551;		Zhou, Chengdong et al.	☐	☐	☐	☐	☐	☐	☐	
9	☑	☐	US 5695622 A	19971209		Electrode for peroxide generator and method for	204/292	204/283; 204/284;		Fraser, Mark E. et al.	☐	☐	☐	☐	☐	☐	☐	
10	☑	☐	US 5647968 A	19970715		Process for making peroxide	205/466	205/468		Fraser, Mark E. et al.	☐	☐	☐	☐	☐	☐	☐	
11	☑	☐	US 5599437 A	19970204		Electrolysis of electroactive species using	205/744	205/754; 205/758;		Taylor, E. Jennings et al.	☐	☐	☐	☐	☐	☐	☐	
12	☑	☐	US 5565073 A	19961015		Electrochemical peroxide generator	204/256	204/265; 204/266		Fraser, Mark E. et al.	☐	☐	☐	☐	☐	☐	☐	

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	Document ID	Pages	1	2	3		5	U	S	C	P	Kind Codes	Sou
1	US 6402931 B1	18							☑				USPAT
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3	US 6309528 B1	12						☑					USPAT
4	US 6303014 B1	24						☑					USPAT
5	US 6210555 B1	14						☑					USPAT
6	US 6203684 B1	11						☑					USPAT
7	US 6080504 A	10						☑					USPAT

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DOCUMENT-IDENTIFIER:  US 6402931 B1
TITLE: Electrochemical machining using modulated reverse electric fields



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INZZ:
Taylor; E. Jennings
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to provide a total anodic on-time of 20 seconds. The voltage during the forward (anodic) pulse was 20 volts, while the voltage during the reverse (cathodic) pulse was three volts. The parameters of the experiments are set forth in Table 3 below.

TABLE 3

Test No.	Current type	Anodic time (ms)	Cathodic time (ms)	Off time	Gap (mm)	Temp (° F.)	Flow rate (gal/min)	Current range (A)
1	DC				0.325	100	1.6	53–63
2	PC	30		10	0.325	100	1.6	61–72
3	MRC	30	10		0.325	100	1.6	69–92
4	DC				0.525	110	2.0	41–45
5	PC	40		20	0.525	110	2.0	46–65
6	MRC	40	20		0.525	110	2.0	49–55
7	MRC	40	20		0.325	100	1.6	75–84
8	MRC	50	20		0.425	110	1.8	55–72

After each experiment the thickness of material removed was determined by measuring the depth of the depression in the surface of the coupon produced by the experiment. The surface of the electropolished area of the workpiece 402 was visually evaluated for shininess and smoothness. The surface roughness was quantitatively evaluated with a profilometer (SURFTEST SV502). The surface roughness measured by the profilometer is expressed as an Ra value, defined as the arithmetic mean of the absolute value of the distance from the mean line to the profile. The results of the experiments are set forth in Table 4 below and in FIGS. 12A, 12B, 13A, 13B, 14A, and 14B, which are photomicrographs showing the surfaces produced by certain of the experiments. Based on the flow pattern of the electrolyte, the electrochemically polished surface was divided into two regions for surface quality evaluation, as indicated in FIG. 11. The central area of the test surface where the electrolyte flow impinges directly on the workpiece surface 410 is identified in Table 4 and FIG. 11 as the P-area 418. The annular area surrounding the P-area 418, where the electrolyte flow is generally parallel to the workpiece surface 410, is identified in Table 4 and FIG. 11 as the J-area 420.

TABLE 4

Test No.	Current type	Surface quality (visual) P-area	Surface quality (visual) J-area	Micro-defects (Number of pits per field 0.64 mm²) P-area	Micro-defects J-area	Surface roughness (Ra) (μm) P-area	Surface roughness (Ra) (μm) J-area	Depth of material removed (μm)
1	DC	+-	+-	22	56	0.51		100–150
2	PC	+-	++	33	56	0.57		100–150
3	MRC	++	++	28	30	0.47		100–150
4	DC	+-	+-	27	36	0.13	0.36	50–130
5	PC	+-	+-	25	23	0.23	0.45	90–130
6	MRC	+-	++	20	16	0.20	0.24	90–130
7	MRC	++	++	18	22			100–140
8	MRC	++	++	10	23			100–130

++ = shiny and smooth
+- = semi-shiny and smooth

The data establish that the surface formed by electropolishing using MRC is generally superior to that formed by either DC or PC electrochemical polishing. It is notable that the surface roughness for PC is generally greater than for DC, i.e., the surface quality is inferior. On the other hand MRC produces a surface that is smoother than either DC or PC electrochemical polishing. The superior quality of the surface achieved with MRC electrochemical polishing is also seen in the fewer number of defects and the general visual appearance of the surface, which appears smooth and shiny. The appearance of the surfaces prepared by DC, PC and MRC can also be compared by referring to FIGS. 12A, 12B, 13A, 13B, 14A and 14B. FIGS. 12A and 12B are micrographs at 200x of the P-area and J-area, respectively of the surface achieved using DC. FIGS. 13A and 13B are micrographs at 200x of the P-area 418 and J-area 420, respectively of the surface achieved using PC. FIGS. 14A and 14B are micrographs at 200x of the P-area and J-area, respectively of the surface achieved using MRC. A comparison of the micrographs readily reveals that the smoothest surface is achieved by using modulated reverse current (MRC).

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for electrochemical deburring of a metal substrate comprising

interposing an electrolyte between a metallic substrate including burrs and an electrically conductive tool, and

passing an electric current between said tool and said substrate to effect anodic dissolution of said burrs,

wherein said electric current is a pulsed current comprised of anodic pulses and cathodic pulses wherein said cathodic pulses are interposed between at least some of said anodic pulses, said anodic pulses have a pulse width of from about 1 ms to about 50 ms and said anodic pulses have a frequency between about 5 Hertz and about 500 Hertz.

2. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

3. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

4. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses and between said cathodic pulses and succeeding anodic pulses.

5. The method of claim 1 wherein said cathodic pulses and said cathodic pulses succeed each other without intervening intervals of no electric current flow.

6. The method of claim 1 wherein said anodic pulses have a frequency between about 10 Hertz and about 300 Hertz.

7. The method of claim 1 wherein said anodic pulses have a frequency between about 10 Hertz and about 100 Hertz.

8. The method of claim 1 wherein said anodic pulses have a pulse width of from about 1 ms to about 30 ms.

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7	US 6080504 A	10	☐	☐	☐	☐	☐	☑	☐	☐	☐		USPAT

DOCUMENT-IDENTIFIER: US 6319384 B1
TITLE: Pulse reverse electrodeposition for metallization and planarization of semiconductor substrates

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INZZ:
Taylor; E. Jennings

damascene-prepared surface wherein the thickness of the metal layer deposited on the surface portions of semiconductor wafers metallized by the process of the invention will be no greater than the depth of metal deposited in the trenches. Preferably, the thickness of the surface layer will be substantially less than the depth of metal deposited in the trenches, e.g., no greater than about 80% of the depth of metal deposited in the trenches. More preferably, the thickness of the surface metal layer will amount to only about 50%, or 20%, or even 10% or less of the depth of metal deposited in the trenches.

The process of the invention can also be applied to deposition of a uniform metal layer on the surface of a semiconductor wafer, as is required for some manufacturing procedures. The application of the process of the invention to such wafers is illustrated in FIGS. 4A–4D.

FIG. 4A illustrates schematically a cross-section of a semiconductor wafer that has been cut from a single crystal of a semiconductor, e.g., silicon. Such wafers are typically round and very thin. In order to metallize the surface of the wafer a barrier layer (not shown) and a very thin conducting layer (not shown) are deposited, e.g., by CVD, as for the case of the damascene-prepared surface discussed above.

When a metal is deposited on the surface of such a wafer, the non-uniform distribution of current at the edges of the wafer gives rise to excess metal deposition at the edge. The excess metal causes the surface of the plated wafer to be somewhat nonplanar, and can interfere with subsequent manufacturing operations unless it is removed or prevented.

In order to avoid the problem of excess metal deposition at the edge of the wafer 400 without resorting to the use of auxiliary electrodes ("robbers"), shields positioned in the electroplating bath, or the like, the plating can be conducted using modulated reverse electric fields according to the invention.

FIG. 4B shows an enlarged cross section of the edge of the wafer 400 as indicated by the circle 4B in FIG. 4A. A metal layer 406 is shown schematically and with exaggerated thickness as deposited on the surface 402 of the wafer 400 near its edge 404 after the first, relatively short, cathodic current pulse. As discussed above for the damascene-prepared surface, because the cathodic pulse is of finite duration, there may be some non-uniformity in the deposition of the metal layer, as shown by the excess metal 408 deposited at the edge 404 of the wafer 400.

FIG. 4C shows schematically the configuration of the deposited metal layer after a subsequent anodic pulse of relatively long duration. Such a long anodic pulse will remove metal non-uniformly and preferentially from the elevated and/or convex portions of the wafer surface. Accordingly, the excess metal 408 that may have been deposited by the cathodic pulse tends to be removed by a subsequent anodic pulse.

FIG. 4D shows schematically the plated metal layer 406 at the edge 404 of the wafer 400 after the plating has been completed. The plated layer 406 ideally extends smoothly and with essentially constant thickness to the edge of the wafer. Furthermore, the plated metal layer 406 will also tend to fill any microscopic depressions in the surface 402 of the wafer 400.

The method of the invention may be used with any metal that can be deposited by electroplating techniques. Thus copper, silver, gold, zinc, chromium, nickel, and alloys thereof such as bronze, brass, and the like, may be applied to microrough surfaces by the process of the invention. The invention is particularly useful in filling trenches and vias in

damascene-prepared surfaces generated in the manufacture of VLSI semiconductor devices and the like and in preparing planar layers of metal on large-diameter semiconductor wafers.

The electroplating bath used in the process of the invention can be any conventional electroplating bath appropriate for the metal being plated. For electroplating copper onto a semiconductor surface, particularly when preparing microscopic conductors by the damascene process, it is preferred to avoid conventional additives such as leveling agents and the like to the extent possible, in order to avoid the difficulties of using, such additives such as possible inclusion in the plated conductors. A preferred bath for electroplating copper onto a microrough surface is an aqueous acidic copper sulfate bath incorporating about 40 to about 80 g/L of copper sulfate, a molar ratio of sulfuric acid to copper sulfate of about 5:1 to about 6:1, about 5% of polyethylene glycol and about 30 ppm to about 60 ppm of chloride ion. A pulse train frequency of about 1000 Hz with a cathodic duty cycle of about 20%, an anodic duty cycle of about 75% and a cathodic/anodic charge transfer ratio of 5 or less appeared to give superior results.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for depositing a smooth layer of a metal onto a microrough substrate comprising

immersing an electrically conductive substrate having a microrough surface in an electroplating bath containing ions of a metal to be deposited onto said surface, said plating bath being substantially devoid of levelers,

immersing a counter electrode in said plating bath

passing an electric current between said substrate and said counterelectrode,

wherein

said electric current is a modulated reversing electric current comprising a train of pulses that are cathodic with respect to said substrate and pulses that are anodic with respect to said substrate,

said cathodic pulses have a duty cycle less than about 50% and said anodic pulses have a duty cycle greater than about 50%

the charge transfer ratio of said cathodic pulses to said anodic pulses is greater than one, and

the frequency of said train of pulses ranges from about 10 Hertz to about 12000 Hertz.

2. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

3. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

4. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and succeeding cathodic pulses.

5. The method of claim 1 wherein said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

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DOCUMENT-IDENTIFIER: US 6309528 B1
TITLE: Sequential electrodeposition of metals using modulated electric fields for manufacture of circuit boards having features of different sizes

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INZZ:
Taylor; E. Jennings

electroplating apparatus and plated in two steps according to the invention. The plating bath had the following composition: 60–65 g/L of copper sulfate, 166 g/L of sulfuric acid, about 50 parts per million (ppm) of chloride ion, and about 300 ppm of polyethylene glycol (PEG).

In the first step of the plating process the pulsed reversing electric current had the following characteristics:

cathodic duty cycle, 33%; anodic duty cycle, 67%; average cathodic current density, 25 amperes per square foot (ASF), frequency of pulse train, about 333 Hz, and cathodic/anodic charge ratio (Q_c/Q_a), 2.5. The plating was conducted for a period of 3 hours in the first step.

The second step of the plating process was then conducted by merely changing the waveform of the plating current. The bath was not changed, the board was not removed from the plating apparatus and no other processing steps were conducted.

In the second step of the plating process the pulsed reversing electric current had the following characteristics: cathodic duty cycle, 90%; anodic duty cycle, 10%; average cathodic current density, 25 amperes per square foot (ASF), frequency of pulse train, about 100 Hz, and cathodic/anodic charge ratio (Q_c/Q_a) 10. The plating was conducted for a period of 1 hour in the second step.

The results achieved are illustrated in FIGS. 4–6. FIG. 4 is a photomicrograph of a cross-section of the plated substrate showing the vias filled with deposited copper. (Certain defects in the brass test panel are also visible.) FIGS. 5 and 6 are photomicrographs showing cross sections of the substrate at each end of the through hole showing a generally uniform plating of the surface of the substrate and the interior surface of the through-hole, with minimum excessive plating ("dogboning") at the edge of the hole.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for depositing a continuous layer of a metal onto a substrate having both hydrodynamically inaccessible recesses and hydrodynamically accessible recesses on its surface comprising

immersing as an electrode an electrically conductive substrate having a generally smooth surface having both at least one hydrodynamically inaccessible recess and at least one hydrodynamically accessible recess in said surface in an electroplating bath containing ions of a metal to be deposited onto said surface,

immersing a counter electrode in said plating bath,

in a first electroplating step, passing a first modulated reversing electric current between said electrodes, wherein

said first modulated reversing electric current comprises first cathodic pulses and first anodic pulses,

said first cathodic pulses have a duty cycle less than about 50% and said first anodic pulses have a duty cycle greater than about 50%,

the charge transfer ratio of said first cathodic pulses to said first anodic pulses is greater than one, and

the frequency of said first pulses ranges from about 10 Hertz to about 12000 Hertz; and

in a second electroplating step, passing a second modulated reversing electric current between said electrodes, wherein

said second modulated reversing electric current comprises second cathodic pulses and second anodic pulses,

said second cathodic pulses have a duty cycle greater than about 50% and said second anodic pulses have a duty cycle less than about 50%,

the charge transfer ratio of said second cathodic pulses to said second anodic pulses is greater than one, and

the frequency of said second pulses ranges from about 10 Hertz to about 5000 Hertz.

2. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses in said first and second electroplating steps.

3. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses in said first and second electroplating steps.

4. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and succeeding cathodic pulses in said first and second electroplating steps.

5. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

6. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 50 Hertz and about 10000 Hertz.

7. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 100 Hertz and about 6000 Hertz.

8. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 500 Hertz and about 4000 Hertz.

9. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses have a duty cycle of from about 30% to about 1%.

10. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses have a duty cycle of from about 30% to about 15%.

11. The method of claim 1 wherein, in said first electroplating step, said cathodic pulses have a duty cycle of from about 30% to about 20%.

12. The method of claim 1 wherein, in said first electroplating step, said anodic pulses have a duty cycle of from about 60% to about 99%.

13. The method of claim 1 wherein, in said first electroplating step, said anodic pulses have a duty cycle of from about 70% to about 85%.

14. The method of claim 1 wherein, in said first electroplating step, said anodic pulses have a duty cycle of from about 70% to about 80%.

15. The method of claim 1 wherein said metal is selected from the group consisting of copper, silver, gold, zinc, chromium, nickel, tin, lead, bronze, brass, solder, and alloys thereof.

16. The method of claim 1 wherein, in said first electroplating step, a layer of metal of substantially uniform thickness is deposited on said surface and within said hydrodynamically isolated recess.

17. The method of claim 1 wherein, in said first electroplating step, the thickness of the metal layer deposited

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3	US 6309528 B1	12	☐	☐	☐	☐	☐	☐	☑	☐	☐		USPAT
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5	US 6210555 B1	14	☐	☐	☐	☐	☐	☑	☐	☐	☐		USPAT
6	US 6203684 B1	11	☐	☐	☐	☐	☐	☑	☐	☐	☐		USPAT
7	US 6080504 A	10	☐	☐	☐	☐	☐	☑	☐	☐	☐		USPAT

DOCUMENT-IDENTIFIER: US 6303014 B1
TITLE: Electrodeposition of metals in small recesses using modulated electric fields

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INZZ:
Taylor; E. Jennings

cycle 78% (anodic on-time (t_a) 156–195 microseconds), average cathodic current density (i_cD_c) about 30 amperes per square foot (ASF)

Waveform 2: 9000 Hz, cathodic duty cycle 40–45% (cathodic on-time (t_c) 44–51 microseconds), anodic duty cycle 55–60% (anodic on-time (t_a) 61–67 microseconds), average cathodic current density (i_cD_c) about 30 amperes per square foot (ASF).

The plating was conducted for periods ranging from 210 to 300 seconds as indicated below.

The experimental conditions are summarized in Table 2 below.

TABLE 2

Ex.	Trench width (μ)	Plating Bath	Rotation Speed (rpm)	Waveform	Time (sec)	Cathodic peak current (mA)	Anodic peak current (mA)	Applied Charge ratio $\frac{Q_c}{Q_a}$
7	0.25	1	400	1	300	425	150	1.2
8	0.25	2	400	1	240	425	125	0.96
9	0.25 & 1.0	1	400	2	240	250	125	1.3
10	0.25	2	400	2	210	250	150–175	1.11
11	0.25	2	800	2	210	250	175	0.95

Cross sections of the trenches in the plated wafers were exposed by focused ion beam (FIB) excavation, and micrographs were prepared using a scanning electron microscope (SEM).

FIG. 12 shows a cross-section of the plated trenches of Example 7. The trenches, having an aspect ratio of about 2, are fully filled and the thickness of the surface deposit is no greater than the depth of the trenches.

FIG. 13 shows a cross-section of the plated trenches of Example 8. The trenches, having an aspect ratio of about 2, are conformally coated with a thin surface deposit.

FIG. 14 shows a cross-section of the plated trenches of Example 9. The trenches, having widths of 0.25 micrometers and 1 micrometer and a depth of about 0.6–0.7 micrometer, are fully filled with a surface plating thickness significantly less than the depth of the trenches.

FIG. 15 shows a cross-section of the plated trenches of Example 10. The surface plating is of moderate thickness.

FIG. 16 shows a cross-section of the plated trenches of Example 11. The trenches have a conformal coating and the surface plating is thin.

EXAMPLE 12

This example illustrates filling of trenches having a width of about 10 micrometers.

Test coupons made from silicon wafers were prepared as in Examples 7–11, having V-shaped trenches having a top width of about 10 micrometers and a depth of about 5 micrometers. The coupons were plated in an apparatus similar to that used for Examples 7–11 for a period of 38 minutes in a bath similar to that of Example 7, using pulse reverse electric filed having a frequency of about 3500 Hz with excursions between about 2950 Hz and about 4969 Hz, a catodic duty cycle of about 14.7%–16.7%, an anodic duty cycle of about 85.3%–83.3%, a cathodic on time of about 0.044–0.058 ms, a charge ration of about 1.16, a peak cathodic current of about 480 mA, an anodic peak current of about 80 mA, and an average current of about 11 mA. FIG. 17 shows a cross-section of the plated trenches. The trenches are fully filled and the surface plating is much thinner than the depth of the trenches.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for depositing a continuous layer of a metal onto a substrate having small recesses in its surface comprising

immersing an electrically conductive substrate having a generally smooth surface having at least one small recess therein wherein at least one transverse dimension of said recess is from about 5 micrometers to about 350 micrometers, in an electroplating bath containing ions of a metal to be deposited onto said surface, said electroplating bath being substantially devoid of at least one member selected from the group consisting of levelers and brighteners,

immersing a counter electrode in said plating bath

passing an electric current between said substrate and said counter electrode,

wherein

said electric current is a modulated reversing electric current comprising pulses that are cathodic with respect to said substrate and pulses that are anodic with respect to said substrate,

said cathodic pulses have a duty cycle less than about 50% and said anodic pulses have a duty cycle greater than about 50%,

the charge transfer ratio of said cathodic pulses to said anodic pulses is greater than one, and

the frequency of said train of pulses ranges from about 10 Hertz to about 12000 Hertz.

2. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

3. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

4. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and succeeding cathodic pulses.

5. The method of claim 1 wherein said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

6. The method of claim 1 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 50 Hertz and about 10000 Hertz.

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DOCUMENT-IDENTIFIER: US 6210555 B1
TITLE: Electrodeposition of metals in small recesses for manufacture of high density interconnects using reverse pulse plating

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Taylor; E. Jennings

reliable, low-resistance interconnection between the conductive copper layer on the surface and the bottom of the recess.

EXAMPLE 3

This example illustrates electrodeposition of copper on a brass substrate having a small recess using modulated reverse electric field, of relatively low frequency, having a relatively long cathodic duty cycle and a relatively short anodic duty cycle. Such a waveform is representative of the modulated reverse electric fields that have been used in some processes for plating through-holes in printed circuit boards.

Copper was deposited on a brass coupon having a drilled hole with a diameter of about 102 micrometers using a modulated reverse electric field. The waveform comprised alternating cathodic and anodic pulses. The period T of the pulse train was 10.2 ms (frequency 98.13 Hz):the cathodic on-time t_c was 9.2 ms and the anodic on-time was 1 ms, resulting in a cathodic duty cycle Dc of 90.2% and an anodic duty cycle of 9.8%. The ratio of cathodic current to anodic current (I_c/I_a) was 0.5 and the ratio of cathodic charge transfer to anodic charge transfer Q_c/Q_a was 5. The average current density was 32.3 mA/cm^2 (30 A/ft^2). The plating was conducted for a period of 3 hours.

The coupon was then sectioned and photographed as in Example 1. A photomicrograph of the plating achieved with this waveform is shown in FIG. 6. The modulated reverse electric field waveform having a long cathodic duty cycle and short anodic duty cycle produced a copper deposit that was confined almost exclusively to the surface. very little copper was deposited in the recess leaving a large void volume within the recess and little or no copper deposit on the lower sides and bottom of the recess.

Evidently such a distribution of plated copper does not provide a reliable interconnection between the conductive copper layer on the surface and the bottom of the recess.

EXAMPLE 4

This example illustrates electrodeposition of copper on a brass substrate having a small recess using modulated reverse electric field having a relatively long cathodic duty cycle and a relatively short anodic duty cycle at a higher frequency than in Example 3. Such a waveform is representative of the modulated reverse electric fields that have been used in some processes for plating through-holes in printed circuit boards, but the frequency is substantially higher than that used in the conventional modulated reverse electric field plating methods.

Copper was deposited on a brass coupon having a drilled hole with a diameter of about 102 micrometers using a modulated reverse electric field. The waveform comprised alternating cathodic and anodic pulses. The period T of the pulse train was 0.382 ms (frequency 2617 Hz), the cathodic on-time t_c was 0.054 ms, and the anodic on-time was 0.054 ms, resulting in a cathodic duty cycle D_c of 86% and an anodic duty cycle D_a of 14%. The ratio of cathodic current to anodic current (I_c/I_a) was 0.5 and the ratio of cathodic charge transfer to anodic charge transfer Q_c/Q_a was 3. The average current density was 32.3 mA/cm^2 (30 A/ft^2). The plating was conducted for a period of 3 hours.

The coupon was then sectioned and photographed as in Example 1. A photomicrograph of the plating achieved with this waveform is shown in FIG. 7. The high-frequency modulated reverse electric field waveform having a long

cathodic duty cycle and short anodic duty cycle produced a copper deposit that was superior to that produced by the very similar low-frequency waveform. However, the thickness of the copper deposit in the lower portion of the recess was substantially thinner than that on the surface of the coupon, and the plating was nonuniform at the mouth of the recess.

Although copper deposit of this example shows a continuous film of copper over the surface of the coupon and into the recess, the film exhibits excessive thickness on the surface of the coupon, and the nonuniform plating at the mouth of the recess suggests the possibility of trapping impurities in the cavity.

EXAMPLES 5 and 6

This example illustrates electrodeposition of copper on a brass substrate having a small recess using modulated reverse electric field according to the invention. The waveform exhibits a relatively short cathodic duty cycle and a relatively long anodic duty cycle.

Copper was deposited on a brass coupon having a drilled hole with a diameter of about 102 micrometers using a modulated reverse electric field. The waveform comprised alternating cathodic and anodic pulses. The period T of the pulse train was 0.293 ms (frequency 3413 Hz), the cathodic on-time t_c was 0.043 ms, and the anodic on-time was 0.25 ms, resulting in a cathodic duty cycle D_c of 14.7 and an anodic duty cycle D_a of 85.3%. The peak cathodic current density I_{cpk} was 277 mA/cm^2, and the peak anodic current density I_{apk} was 42 ma/cm^2, resulting in a ratio of cathodic charge transfer to anodic charge transfer Q_c/Q_a of 1.2. The average current density was 15 mA/cm^2 (13.9 A/ft^2). In Example 5, the plating was conducted for a period of 2 hours; in Example 6 the plating was conducted for a period of 4 hours.

The coupons were then sectioned and photographed as in Example 1. A photomicrograph of the plating of Example 5 is shown in FIG. 8; a photomicrograph of the plating of Example 6 is shown in FIG. 9.

In Example 5 (2 hours plating)the copper deposit was relatively uniform over the surface of the coupon and the sides and bottom of the recess. Evidently, such a layer of electrodeposited copper is suitable for providing a reliable electrical connection between a device located at the bottom of a recess and a conductive strip on the surface of the substrate.

In Example 6 (4 hours plating) the copper deposit on the surface of the coupon is still relatively thin. However, the entire recess has been filled with electroplated copper. Accordingly, the process of the invention is capable of producing vias or blind recesses that are filled with copper (stud vias) while avoiding excess deposition of copper on the surface of the substrate.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for depositing a continuous layer of a metal onto a substrate having small recesses in its surface comprising

6/2002

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7	US 6080504 A	10	☐	☐	☐	☐	☐	☑	☐	☐	☐		USPAT

DOCUMENT-IDENTIFIER: US 6210555 B1
TITLE: Electrodeposition of metals in small recesses for manufacture of high density interconnects using reverse pulse plating

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INZZ:
Taylor; E. Jennings.

US 6,210,555 B1

13

immersing an electrically conductive substrate having a generally smooth surface having at least one small recess therein, wherein at least one transverse dimension of said recess is from about 5 micrometers to about 250 micrometers, in an electroplating bath containing ions of a metal to be deposited onto said surface,

immersing a counter electrode in said plating bath

passing an electric current between said substrate and said counterelectrode,

wherein

said electric current is a modulated reversing electric current comprising a train of pulses that are cathodic with respect to said substrate and pulses that are anodic with respect to said substrate,

said cathodic pulses have a duty cycle less than about 50% and said anodic pulses have a duty cycle greater than about 50%,

the charge transfer ratio of said cathodic pulses to said anodic pulses is greater than one, and

the frequency of said pulse train ranges from about 10 Hertz to about 5000 Hertz.

2. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

3. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

4. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and succeeding cathodic pulses.

5. The method of claim 1 wherein said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

6. The method of claim 1 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 50 Hertz and about 5000 Hertz.

7. The method of claim 1 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 100 Hertz and about 3000 Hertz.

8. The method of claim 1 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 500 Hertz and about 1500 Hertz.

9. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 30% to about 1%.

10. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 30% to about 15%.

11. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 30% to about 20%.

12. The method of claim 1 wherein said anodic pulses have a duty cycle of from about 60% to about 99%.

13. The method of claim 1 wherein said anodic pulses have a duty cycle of from about 70% to about 85%.

14. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 70% to about 80%.

15. The method of claim 1 wherein said metal is selected from the group consisting of copper, silver, gold, zinc, chromium, nickel, bronze, brass, and alloys thereof.

16. The method of claim 1 wherein a layer of metal of substantially uniform thickness is deposited on said surface and within said recesses.

17. The method of claim 1 wherein the thickness of the metal layer deposited within said recesses is greater than the thickness of the metal layer deposited on said surface.

18. The method of claim 1 wherein said recesses are substantially filled with metal.

19. The method of claim 1 wherein at least one transverse dimension of said recess is from about 25 micrometers to about 250 micrometers.

14

20. The method of claim 1 wherein at least one transverse dimension of said recess is from about 50 micrometers to about 150 micrometers.

21. The method of claim 1 wherein amounts of conventional plating bath additives that are used in small amounts are minimized in said plating bath.

22. The method of claim 21 wherein said plating bath is essentially devoid of said conventional plating bath additives that are used in small amounts.

23. The method of claim 1 wherein additives in said plating bath that help to produce a level coating of metal are minimized.

24. The method of claim 1 wherein said plating is essentially devoid of additives that help to produce a level coating of metal.

25. The method of claim 1 wherein said metal is copper.

26. The method of claim 25 wherein amounts of conventional plating bath additives that are used in small amounts are minimized in said plating bath.

27. The method of claim 25 wherein said plating bath is essentially devoid of said conventional plating bath additives that are used in small amounts.

28. The method of claim 27 wherein at least one of said small recesses is filled in a single plating step.

29. The method of claim 25 wherein additives in said plating bath that help to produce a level coating of metal are minimized.

30. The method of claim 25 wherein said plating bath is essentially devoid of additives that help to produce a level coating of metal.

31. The method of claim 30 wherein at least one of said small recesses is filled in a single plating step.

32. The method of claim 25 wherein said plating bath contains conventional amounts of copper ions, sulfuric acid, chloride ions, and a conventional polyethylene glycol carrier compound.

33. The method of claim 25 wherein said plating bath consists essentially of an aqueous solution containing conventional amounts of copper ions, sulfuric acid, chloride ions, and a conventional polyethylene glycol carrier compound.

34. The method of claim 33 wherein at least one of said small recesses is filled in a single plating step.

35. The method of claim 25 wherein said plating bath consists of an aqueous solution containing conventional amounts of copper ions, sulfuric acid, chloride ions, and a conventional polyethylene glycol carrier compound.

36. The method of claim 25 wherein said plating bath contains about 55 g/L of copper sulfate, about 9% by weight of sulfuric acid, about 50 parts per million of chloride ions and about 5% by weight of a conventional polyethylene glycol carrier compound.

37. A method for filling a small recess in a surface of an electrically conducting substrate with a void-free deposit of metal comprising

immersing an electrically conductive substrate having a generally smooth surface having at least one small recess therein, wherein at least one transverse dimension of said recess is from about 5 micrometers to about 250 micrometers, in an electroplating bath containing ions of a metal to be deposited onto said surface,

immersing a counter electrode in said plating bath,

passing an electric current essentially continuously between said substrate and said counterelectrode for a period of time until said recess has been filled with said metal,

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7	US 6080504 A	10	☐	☐	☐	☐	☐	☑	☐	☐	☐		USPAT

DOCUMENT-IDENTIFIER: US 6203684 B1
TITLE: Pulse reverse electrodeposition for metallization and planarization of a semiconductor substrates

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copper sulfate bath incorporating about 40 to about 80 g/L of copper sulfate, a molar ratio of sulfuric acid to copper sulfate of about 5:1 to about 8:1, about 5% of polyethylene glycol and about 30 ppm to about 60 ppm of chloride ion. A pulse train frequency of about 1000 Hz with a cathodic duty cycle of about 20%, an anodic duty cycle of about 75% and a cathodic/anodic charge transfer ratio of 5 or less appeared to give superior results.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for depositing a smooth layer of a metal onto a microrough substrate comprising

immersing an electrically conductive substrate having a microrough surface in an electroplating bath containing ions of a metal to be deposited onto said surface,

immersing a counter electrode in said plating bath, passing an electric current between said substrate and said counterelectrode for an essentially continuous period of time until microscopic depressions on said microrough surface have been filled with said metal,

wherein

said electric current is a modulated reversing electric current comprising a train of pulses that are cathodic with respect to said substrate and pulses that are anodic with respect to said substrate,

said cathodic pulses have a duty cycle less than about 50% and said anodic pulses have a duty cycle greater than about 50%,

the charge transfer ratio of said cathodic pulses to said anodic pulses is greater than one, and

the frequency of said pulse train ranges from about 10 Hertz to about 5000 Hertz, and

said plating bath is substantially devoid of leveling agents.

2. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

3. The method of claim 1 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

4. The method of claim 1 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and succeeding cathodic pulses.

5. The method of claim 1 wherein said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

6. The method of claim 1 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 50 Hertz and about 5000 Hertz.

7. The method of claim 1 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 100 Hertz and about 3000 Hertz.

8. The method of claim 1 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 500 Hertz and about 1500 Hertz.

9. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 30% to about 1%.

10. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 30% to about 15%.

11. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 30% to about 20%.

12. The method of claim 1 wherein said anodic pulses have a duty cycle of from about 60% to about 95%.

13. The method of claim 1 wherein said anodic pulses have a duty cycle of from about 70% to about 85%.

14. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 70% to about 80%.

15. The method of claim 1 wherein said metal is selected from the group consisting of copper, silver, gold, zinc, chromium, nickel, bronze, brass, and alloys thereof.

16. The method of claim 1 wherein said metal is copper.

17. The method of claim 1 wherein said bath consists essentially of about 40 g/L to about 80 g/L of copper sulfate, sulfuric acid in a molar ratio of sulfuric acid to copper sulfate of about 5:1 to about 8:1, about 5% by weight of polyethylene glycol and about 30 parts per million to about 60 parts per million of chloride ion.

18. A method for filling a microscopic recess in a surface of an electrically conducting substrate with a void-free deposit of metal comprising

immersing an electrically conductive substrate having a surface and at least one microscopic recess in said surface in an electroplating bath containing ions of a metal to be deposited into said recess, said plating bath being essentially devoid of leveling agents,

immersing a counter electrode in said plating bath, passing an electric current essentially continuously between said substrate and said counterelectrode for a period of time until said recess has been filled with said metal,

wherein

said electric current is a modulated reversing electric current comprising a train of pulses that are cathodic with respect to said substrate and pulses that are anodic with respect to said substrate,

said cathodic pulses have a duty cycle less than about 50% and said anodic pulses have a duty cycle greater than about 50%,

the charge transfer ratio of said cathodic pulses to said anodic pulses is greater than one, and

the frequency of said pulse train ranges from about 10 Hertz to about 5000 Hertz.

19. The method of claim 18 wherein said passage of electric current is terminated promptly when said recess has been filled with said metal.

20. The method of claim 18 wherein said metal is copper.

21. The method of claim 18 wherein said bath consists essentially of about 40 g/L to about 80 g/L of copper sulfate, sulfuric acid in a molar ratio of sulfuric acid to copper sulfate of about 5:1 to about 8:1, about 5% by weight of polyethylene glycol and about 30 parts per million to about 60 parts per million of chloride ion.

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DOCUMENT-IDENTIFIER: US 6080504 A
TITLE: Electrodeposition of catalytic metals using pulsed electric fields

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Taylor; E. Jennings

the form of a continuous web. The web is passed continuously over the surface of the plating bath 306. In the arrangement illustrated in FIG. 4, the web of uncatalyzed gas diffusion electrode is supplied on a supply reel 308. The web passes over guide and contact reel 312 positioned to place the catalyst support layer containing the uncatalyzed catalyst support particles in contact with the surface of plating bath 306. The backing layer 202 of the GDE is in electrical contact with the electrically conductive guide reel 312. Power supply 318 provides voltage for the electrodeposition through terminals 320, connections 322, and contact brush 316 to the guide and contact reel 312 and the counterelectrode 304. The web is moved across the surface of the plating bath at a rate such that it is in contact with the plating bath for a sufficient time for deposition of the predetermined amount of catalytic metal particles. The catalyzed gas diffusion electrode 200 then passes over guide reel 314 and is taken up on take-up reel 310. The gas diffusion electrode web 200 is moved over the surface of the plating bath 306 by drive means not shown acting on one or more of the supply reel 308, take-up reel 310, and/or guide reels 312 and 314. The continuous catalyzed gas diffusion electrode web so prepared may then be used in subsequent operations for the manufacture of fuel cells.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

We claim:

1. A method for depositing nanocrystalline particles of a catalytic metal on a substrate comprising
 immersing an electrically conductive substrate and a counterelectrode in bath containing ions of a metal to be deposited on said substrate;
 passing an electric current between said substrate and counter electrode;
 wherein
 said electric current is a pulsed electric current comprising pulses that are cathodic with respect to said substrate,
 said cathodic pulses have a duty cycle less than about 40%, and
 the frequency of said pulses ranges from about 10 hertz to about 5000 hertz.

2. The method of claim 1 wherein said frequency is between about 50 hertz and about 5000 hertz.

3. The method of claim 1 wherein said frequency is between about 100 hertz and about 3000 hertz.

4. The method of claim 1 wherein said frequency is between about 500 hertz and about 1500 hertz.

5. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 1% to about 30%.

6. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 2% to about 20%.

7. The method of claim 1 wherein said cathodic pulses have a duty cycle of from about 5% to about 15%.

8. The method of claim 1 wherein
 said electric current is a modulated reversing electric current comprising pulses that are cathodic with respect to said substrate and pulses that are anodic with respect to said substrate,

 said cathodic pulses have a duty cycle less than about 40% and said anodic pulses have a duty cycle not greater than about 90%,
 the charge transfer ratio of said cathodic pulses to said anodic pulses is greater than one, and
 the frequency of said pulses ranges from about 10 hertz to about 5000 hertz.

9. The method of claim 8 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses.

10. The method of claim 8 wherein an interval of no electric current flow is interposed between said anodic pulses and succeeding cathodic pulses.

11. The method of claim 8 wherein an interval of no electric current flow is interposed between said cathodic pulses and succeeding anodic pulses and between said anodic pulses and is succeeding cathodic pulses.

12. The method of claim 8 wherein said cathodic pulses and said anodic pulses succeed each other without intervening intervals of no electric current flow.

13. The method of claim 8 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 50 hertz and about 5000 hertz.

14. The method of claim 8 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 100 hertz and about 3000 hertz.

15. The method of claim 8 wherein said cathodic pulses and said anodic pulses form a pulse train having a frequency between about 500 hertz and about 1500 hertz.

16. The method of claim 8 wherein said cathodic pulses have a duty cycle of from about 1% to about 30%.

17. The method of claim 8 wherein said cathodic pulses have a duty cycle of from about 2% to about 15%.

18. The method of claim 8 wherein said cathodic pulses have a duty cycle of from about 5% to about 10%.

19. The method of claim 8 wherein said anodic pulses have a duty cycle of from about 1% to about 90%.

20. The method of claim 8 wherein said anodic pulses have a duty cycle of from about 15% to about 50%.

21. The method of claim 8 wherein said cathodic pulses have a duty cycle of from about 20% to about 40%.

22. The method of claim 1 wherein said catalytic metal is selected from the group consisting of platinum, palladium ruthenium, rhodium, and alloys thereof.

23. A gas diffusion electrode for a proton exchange membrane fuel cell comprising
 a gas-permeable electrically conductive backing layer;
 a catalyst layer supported on said backing layer and comprising
 a particulate, electrically conductive catalyst support in contact with a proton exchange resin and in electrical contact with said backing layer, and
 a catalytic metal in finely divided form in electrical contact with said particulate catalyst support, said catalytic metal being present in the form of fine particles having diameter of from about 3.0 nanometers to about 8.0 nanometers and the loading of said catalyst being from about 0.1 mg/cm^2 to about 1.0 mg/cm^2,
 said particles of catalytic metal having been deposited by the method of claim 1.

24. A method of fabricating a gas diffusion electrode comprising
 1.) providing a gas-permeable electrically conducting backing web;
 2.) coating one major surface of said backing web with a layer of a particulate catalyst support in contact with a proton exchange resin binder;